

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : E21B 43/02, 43/22, C09K 7/02	A1	(11) International Publication Number: WO 99/50529 (43) International Publication Date: 7 October 1999 (07.10.99)
(21) International Application Number: PCT/GB99/00941 (22) International Filing Date: 25 March 1999 (25.03.99) (30) Priority Data: 9806492.6 27 March 1998 (27.03.98) GB (71) Applicant (for all designated States except CA FR US): SOF-ITECH N.V. [BE/BE]; Rue de Stalle, 140, B-1180 Brussels (BE). (71) Applicant (for FR only): COMPAGNIE DES SERVICES DOWELL SCHLUMBERGER S.A. [FR/FR]; 50, avenue Jean Jaurès, F-92541 Montrouge (FR). (71) Applicant (for CA only): SCHLUMBERGER CANADA LIMITED [CA/CA]; 24th floor, Monenco Place, 801 6th Avenue, S.W., Calgary, Alberta T2P 3W2 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): DAVIES, Stephen, Nigel [GB/GB]; 1 Church End, Over, South Cambridgeshire CB4 5NH (GB). JONES, Timothy, Gareth, John [GB/GB]; 242 High Street, Cottenham, Cambridge CB4 8RZ (GB). TUSTIN, Gary, John [GB/GB]; 8 Carrick Close, Cambridge CB1 8RQ (GB).		(74) Agent: MIRZA, Akram, Karim; Schlumberger Cambridge Research Limited, High Cross, Madingley Road, Cambridge CB3 0EL (GB). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: SURFACTANT BASED GELLING COMPOSITION FOR WELLBORE SERVICE FLUIDS		
(57) Abstract A composition, in particular a wellbore service fluid, comprising monomeric surfactants, preferably viscoelastic surfactants, in combination with a polymerization agent. Additionally, the fluid may contain a cross-linking agent to cross-link the polymerized surfactants.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Surfactant based gelling composition for wellbore service fluids

The present invention relates to surfactant, particularly
5 viscoelastic surfactant based gelling compositions preferably
used for wellbore service fluids. More particularly it relates
to such compositions for selectively reducing the flow of
subterranean aqueous fluids into a well while maintaining the
hydrocarbon production.

10

BACKGROUND OF THE INVENTION

15 Various types of wellbore fluids are used in operations related
to the development, completion, and production of natural
hydrocarbon reservoirs. The operations include fracturing
subterranean formations, modifying the permeability of
subterranean formations, or sand control. Other applications
20 comprise the placement of a chemical plug to isolate zones or
complement an isolating operation. The fluids employed by those
operations are known as drilling fluids, completion fluids, work
over fluids, packer fluids, fracturing fluids, conformance or
permeability control fluids and the like.

25

Of particular interest with regard to the present inventions are
fluids for water control applications: During the life cycle of
a hydrocarbon well, e.g., a well for extracting oil or natural
gas from the Earth, the producing well commonly also yields
30 water. In these instances, the amount of water produced from the
well tends to increase over time with a concomitant reduction of
hydrocarbon production. Frequently, the production of water
becomes so profuse that remedial measures have to be taken to
decrease the water/hydrocarbon production ratio. As a final
35 consequence of the increasing water production, the well has to
be abandoned.

- 2 -

In many cases, a principal component of wellbore service fluids are gelling compositions, usually based on polymers or viscoelastic surfactants.

5 There has been considerable interest in the viscoelastic gels formed from the solutions of certain surfactants when the concentration significantly exceeds the critical micelle concentration. Viscoelastic surfactant solutions are usually formed by the addition of certain reagents to concentrated
10 solutions of surfactants, which most frequently consist of long-chain quaternary ammonium salts such as cetyltrimethylammonium bromide (CTAB). Common reagents which generate viscoelasticity in the surfactant solutions are salts such sodium salicylate and sodium isocyanate and non-ionic organic molecules such as
15 chloroform. The electrolyte content of surfactant solutions is also an important control on their viscoelastic behaviour. The viscoelastic properties of a solution arises from the formation of long cylindrical (or "worm-like") micelles and their entanglement to form a three-dimensional structure. The
20 surfactant micelles behave in a manner somewhat similar to polymer chains, although the former are dynamic entities with the surfactant monomers constantly joining and leaving the micelles. The micelles are held together by van der Waals (and other similar) interactions, in contrast to the strong covalent
25 bonds between monomer units in polymers. The surfactant micelles are fragile(4) and the gels formed by the entangled micelles are relatively weak. Such gels are often termed physical gels(6), in contrast to chemical gels which are commonly formed by the cross-linking of high molecular weight polymers using covalent
30 or ionic bonds.

Further references related to the use of viscoelastic surfactants as wellbore service fluids can be found for example in U.S. patents No.4,695,389, No. 4,725,372, No. 5,258,137 and
35 No. 5,551,516.

Several patents have described the use of polymerizable surfactants in emulsion polymerization. In U.S. patent

- 3 -

No.5,162,475, there is described the use of α - β (i.e., terminal) ethylenically unsaturated poly(alkyleneoxy) compounds which act as the surfactant in the emulsion polymerization process and which co polymerize with the non-surfactant monomers. Several
5 earlier patents, U.S. patents No.4,049,608, 4,224,455 and 4,337,185 have also described the co-polymerization of the surfactant monomers used in emulsion polymerization processes. In U.S. patent No.4,064,091 there is described the use of
10 unsaturated quaternary ammonium salts as surfactants in emulsion polymerization processes which co-polymerize with the non-surfactant monomers to produce self-stabilising polymeric dispersions which are free of surfactant monomers.

Most recent work by K. Tauer, published in "Polymeric
15 Dispersions: Principles and Applications" (J.M. Asua ed.), NATO ASI Series E: Applied Sciences Vol. 335, 1997 describes the polymerization of surfactant-like monomers in small micelles in the absence of other surfactants.

20 The object of this present invention is to provide improved compositions, especially for wellbore service fluids, based on monomeric surfactants, particularly monomeric viscoelastic surfactants. It is a specific object of the invention to provide stable gels using such compositions. It is a further specific
25 object of the invention to provide such compositions for water control operations in hydrocarbon wells.

SUMMARY OF THE INVENTION

30

The objects of the invention are achieved by polymerizing monomeric surfactants forming micelles in an aqueous solution.

Herein, monomeric is defined as having no repetitive units.

35 Preferably, the molecular mass of monomeric surfactants is less than 10000, preferably less than 1000 units.

- 4 -

Surfactants are water soluble surface-active materials with a hydrophobic group. The solubility in water is controlled by a hydrophilic group. Surfactants are usually classified according to their electrochemical properties as anionic, cationic or non-ionic agents. Often they are referred to as detergents, soaps or amphiphilic compounds.

In solution (and above a critical concentration) surfactants form micelles. The concentration of the surfactants is sufficient to transform the solution into a gel. Preferably, the concentration lies in the range of 1 to 10 weight per cent.

In a preferred embodiment of the invention the monomeric surfactant belong to the class of surfactant which display in solution viscoelastic behavior.

The polymerizing agent is capable of initiating a polymerization of the surfactants forming a micelle, thus stabilizing the gel. The concentration of the agent is preferably in the range of 10 to 1000 ppm (parts per million)

As applied to solutions, the term "viscoelastic" means a viscous solution which at least partially returns to its original state when an applied stress is released. The property of viscoelasticity can be tested for example by observing whether bubbles created by swirling the sample recoil after the swirling ceased. For this and other test reference is made to H.A. Barnes et al. Rheol. Acta. 14 (1975), pp. 53-60 and S. Gravsholt, Journal of Coll. and Interface Sci. 57(3), 1976, pp.575-6.

The physical gels formed by viscoelastic surfactant solutions can exhibit considerable responsiveness to their external chemical and physical environments. For example, the viscoelasticity of these concentrated surfactant solutions can be destroyed by contact with hydrocarbons and other organic liquids. The viscoelasticity of the solutions can also be lost on heating but recovered on cooling. However, once polymerized,

- 5 -

the polymeric gels formed show significantly less responsiveness to their chemical and physical environment.

Viscoelastic surfactants employed by the current invention are described for example in the above cited U.S. patents No. 4,695,389, No. 4,725,372, and No. 5,551,516 and literature referred to therein.

In a further preferred embodiment of the invention, the polymerized surfactants are cross-linked, thus further enhancing the stability of the gel. The preferred concentration of the cross-linking agent in the solution lies in the range of 10 to 1000 ppm.

Chemical cross-linking is defined as forming a chemical bond between the cross-linked molecules. Chemical cross-linking is understood to be stable and irreversible.

The cross-linking agents can be either inorganic ions (or ionic complexes) or polar organic molecules. When the polymer contains ionic groups such as carboxylate or sulphonate functions the polymer chains can be cross-linked by inorganic ions such as chromium(III) or zirconium(IV), frequently in the presence of monomeric ligands, such as acetate or adipate ions, to control the rate of cross-linking. Alternatively, organic cross-linking agents, such as hexanal or heptanal, can be used.

These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description following below.

MODE(S) FOR CARRYING OUT THE INVENTION

35

The polymerization and cross-linking of the cylindrical micelles in viscoelastic surfactant solutions is illustrated with three examples. The polymerization in the three examples is achieved

- 6 -

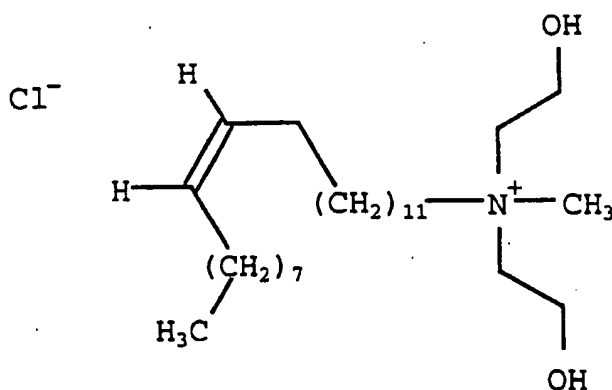
by a free radical mechanism. However, it is stressed that the polymerization of the surfactant monomers to form polymeric surfactants can be achieved by a number of well known methods, including ring-opening polymerization, cation polymerization and anionic polymerization techniques. A description of these and other polymerization techniques has been given by G. Odian in : "Principles of Polymerization", 3rd ed., pp., Wiley, New York (1991).

10

Example 1

The first example is the polymerization of the surfactant N-erucyl-N,N-bis(2-hydroxyethyl)-N-methylammonium chloride

15



in an aqueous solution. The polymerization of the surfactant molecules is achieved by joining the carbon-carbon double bonds by a free radical polymerization reaction within the micelles using the following processes.

A viscoelastic surfactant solution was produced using 30 g/l of the surfactant N-erucyl-N,N-bis(2-hydroxyethyl)-N-methylammonium chloride with 40 g/l ammonium chloride. A volume of 100 ml of the viscoelastic surfactant solution was placed in a bottle which was purged with dry nitrogen gas to remove any dissolved oxygen. After sufficient purging 10 mg of the free radical initiator 2,2'-azo(bis-amidinopropane)dihydrochloride was added to the viscoelastic surfactant solution and mixed thoroughly.

- 7 -

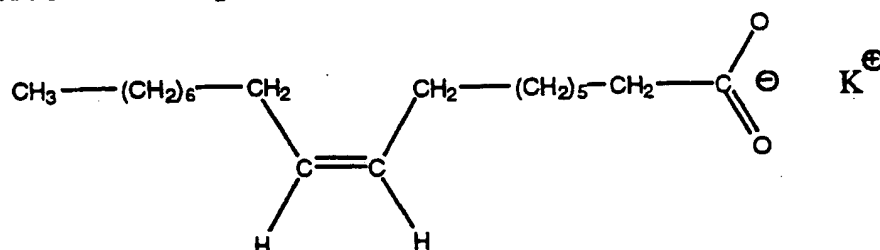
The surfactant solution was heated at 60°C for 24 hours under an atmosphere of nitrogen. Polymerization of the surfactant monomers in the giant micelles resulted in the viscosity of the gel becoming insensitive to contact with hydrocarbon. The viscosity of the surfactant gel was not altered by polymerization of the surfactant monomers. The polymerized surfactant gel retained its gel strength after prolonged contact with water.

10

Example 2

The second example is the polymerization of the viscoelastic surfactant solution formed by potassium oleate in a potassium chloride electrolyte solution:

15

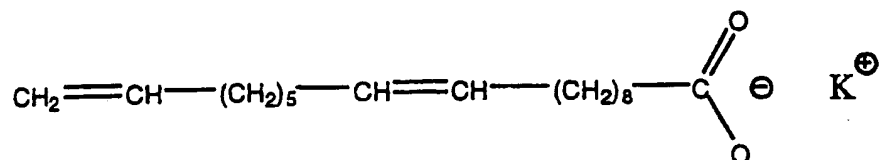


The viscoelastic surfactant solution was formed by mixing 60 g/l potassium oleate with 60 g/l potassium chloride. A sample of 100 ml of the viscoelastic surfactant solution was purged with nitrogen and mixed with 10 mg of the initiator 2,2'-azo(bisamidinopropane)dihydrochloride. The solution was heated at 60°C for 24 hours under an atmosphere of nitrogen. The resulting solution of polymerized surfactants was slightly less viscoelastic than the original monomeric solution but the observed viscoelasticity was insensitive to contact with hydrocarbon. The gel formed by the polymerized surfactant retained its viscoelasticity after prolonged contact with water

30

Example 3

The third example is the polymerization of a long-chain vinyl surfactant, the potassium salt of 10,17-octadecyldienoic acid



5 in a viscoelastic solution. The surfactant monomer is synthesized by a two stage reaction which involves coupling of the short-chain vinyl surfactant 10-undecenoic acid to 8-bromo-1-octene. The first stage consists of reacting the 10-undecenoic
10 acid with ozone in dichloromethane followed by treatment with dimethyl sulphide (DMS) at -78°C to convert the carbon-carbon double bond to a terminal aldehyde group by the so-called oxo-uncoupling reaction. The second stage consists of reacting the
15 8-bromo-1-octene with triphenylphosphine in dichloromethane to form 8-triphenylphosphonium-1-octene bromide which is then coupled with the aldehyde carboxylic acid and butyllithium in tetrahydrofuran by the Wittig reaction to form the surfactant monomer as shown above.

20 The potassium salt of 10,17-octadecyldienoic acid forms a viscoelastic surfactant solution at a concentration of 60 g/l in the presence of 40 g/l ammonium chloride. The surfactant monomers were polymerized using 10 mg of the free radical initiator 2,2'-azo(bis-amidinopropane)dihydrochloride in 100 ml
25 of viscoelastic surfactant solution which had been purged with nitrogen gas. The solution was heated at 60°C for 24 hours under an atmosphere of nitrogen.

Polymerization of the surfactant resulted in a rigid gel which
30 retained the viscoelasticity of the original (monomeric) surfactant solution but showed none of its sensitivity to contact with hydrocarbon or water.

In all three of the examples given above it is possible to
35 cross-link the polymeric micelles to increase the gel strength and to reduce further any sensitivity of the gel to its chemical

- 9 -

and physical environment. The carboxylated polymers shown in the three above examples can be cross-linked using a polyvalent metal ion, such as chromium(III) or zirconium(IV) ions.

Similarly, if the terminal carboxylate groups are replaced by sulphonate groups, then the polymerized micelles can also be cross-linked with metal ions such as zirconium(IV).

Alternatively, the original viscoelastic surfactant solution can be composed of two different types of surfactant monomer which form mixed cylindrical micelles. The second surfactant monomer can be chosen to give a required cross-linking functionality to the polymerized micelle. For example, a viscoelastic surfactant solution can be formed with 10,17-octadecyldienoic acid and its amide 10,17-octadecyldienamide added in the mole fraction ratio of approximately 0.98:0.02. The two surfactants can be polymerized, as in example 3 given above, to yield a co-polymerized micelle. The amide groups within the polymerized micelles can be used to cross-link them with organic cross-linking agents such as formaldehyde and phenol. The high concentration of surfactant in the aqueous solution can be used to solubilise otherwise insoluble long-chain cross-linking agents such as hexanal or octanal. Other cross-linking functional groups can be envisaged.

- 10 -

CLAIMS

1. A wellbore service fluid comprising monomeric surfactants and a polymerization agent in an aqueous solution.
- 5 2. The fluid of claim 1, wherein the monomeric surfactants are viscoelastic.
3. The fluid of claim 1, wherein the polymerization agent is a
10 radical, a cationic, or an anionic initiator.
4. The fluid of claim 1, further comprising a cross-linking agent.
- 15 5. Composition comprising monomeric viscoelastic surfactants forming micelles in said composition and an agent polymerizing said surfactants.
6. The composition of claim 5, further comprising a cross-
20 linking agent cross-linking the polymerized surfactants.
7. Method of stabilizing a viscoelastic gel comprising surfactants characterized in that said surfactants are polymerized.
- 25 8. The method of claim 7, further comprising the step of crosslinking the polymerized surfactants.

30

INTERNATIONAL SEARCH REPORT

national Application No

PCT/GB 99/00941

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 E21B43/02 E21B43/22 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 582 137 A (SCHMITT KIRK D) 15 April 1986 see column 2, line 41 - line 54; claims 1-9 see column 5, line 34 - line 47; example 1	1-8
Y	see the whole document	1-8
X	US 4 721 161 A (RICHARDSON WILLIAM C ET AL) 26 January 1988 see column 2, line 5 - line 28; claims 1-24 see column 5, line 29 - line 41	1-8
Y	see the whole document	1-8
X	US 4 284 517 A (CHEN CATHERINE S H ET AL) 18 August 1981 see claims 1-8; examples 1-4	7
A	see the whole document	1-6,8
	--- -/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

25 June 1999

Date of mailing of the international search report

07/07/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

olde Scheper, B

INTERNATIONAL SEARCH REPORT

national Application No

PCT/GB 99/00941

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 317 893 A (CHEN CATHERINE S H ET AL) 2 March 1982 see claims 1-8; examples 1-4	7
A	see the whole document	1-6,8
X	US 5 021 526 A (BALL LAWRENCE E) 4 June 1991 see claims 1-3	7
A	see the whole document	1-6,8
X	US 5 039 433 A (SOPKO THOMAS M ET AL) 13 August 1991 see column 6, line 37 - line 39	7
A	see the whole document	1-6,8
Y	US 5 551 516 A (NORMAN WILLIAM D ET AL) 3 September 1996 cited in the application see column 4, line 65 - column 5, line 38 see column 6, line 8 - line 12 see column 7, line 11 - line 14 see column 8, line 39 - line 42 see column 9, line 21 - line 34; claims 1-6	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/GB 99/00941

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4582137	A	15-04-1986	NONE	
US 4721161	A	26-01-1988	NONE	
US 4284517	A	18-08-1981	US 4317893 A	02-03-1982
US 4317893	A	02-03-1982	US 4284517 A	18-08-1981
US 5021526	A	04-06-1991	NONE	
US 5039433	A	13-08-1991	US 4812544 A	14-03-1989
			AT 119920 T	15-04-1995
			AU 601700 B	20-09-1990
			AU 6338486 A	24-03-1987
			BR 8606876 A	03-11-1987
			CA 1268293 A	24-04-1990
			CN 1010684 B	05-12-1990
			CN 1050029 A	20-03-1991
			DE 3650269 D	20-04-1995
			DE 3650269 T	27-07-1995
			DK 234587 A	08-05-1987
			EP 0235276 A	09-09-1987
			EP 0628576 A	14-12-1994
			FI 871957 A, B	04-05-1987
			IN 167018 A	18-08-1990
			JP 2517574 B	24-07-1996
			JP 63500726 T	17-03-1988
			MX 165892 B	09-12-1992
			RU 2011653 C	30-04-1994
			WO 8701377 A	12-03-1987
US 5551516	A	03-09-1996	NONE	